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## CERAMIC MIXTURES FOR MANUFACTURING FLOOR TILE

N. A. Mikhailova,<sup>1</sup> E. A. Gryadkina,<sup>1</sup> Z. S. Martem'yanova,<sup>1</sup> and T. Yu. Kolesnikova<sup>1</sup>Translated from *Steklo i Keramika*, No. 4, pp. 20–22, April, 1998.

It is shown that fully sintered ceramic mixtures for floor tile can be obtained from Berlin clay with addition of pegmatite from the Chupinskoe and Vishnevogorskoe deposits. The phase composition and microstructure of the synthesized materials are described.

In Russia, ceramic floor tile is produced in correspondence with the requirements of GOST 6787–90 State Standard. The water absorption of the tile should not exceed 4%. At the present time, the building industry demands floor tile without open porosity and with zero water absorption. Such tile possesses high technical characteristics and can be polished, which improves considerably the appearance of the structures.

As a rule, ceramic tile for floors is produced from mixtures that contain 80% plastic components and 20% fluxes (here and below in mass fractions) [1, 2]. In order to obtain fully sintered ceramic mixtures, we studied compositions with a much higher content of fluxes (50–70%).

The ceramics industry does not use mixtures with such a high flux content, because in addition to the positive sintering action, the fluxes can have a negative effect, i.e., increase the susceptibility of the products to deformation and increase the closed porosity.

We tested the raw components used by the Ekaterinburg Ceramic Plant, namely, Berlin clay and Chupinskoe and Vishnevogorskoe pegmatite. The chemical composition of these materials is presented in Table 1.

We began with a study of some properties of the initial components. The properties of Berlin clay were studied in [3]. The thermogram of the Berlin clay obtained by us is presented in Fig. 1.

In deciphering the DTA data, we established that the predominant clay mineral is kaolinite (the endothermic effect at 578°C caused by removal of chemically bound water from the kaolinite and the exothermic effect at 940°C connected with rearrangement of the metakaolinite lattice).

The Berlin clay also contains montmorillonite (endothermic effect of removal of adsorption water at 185°C). Our

data on the mineralogical composition of the Berlin clay coincide with the results of [3], i.e., the Berlin clay has a kaolinite-montmorillonite composition. We used the method in [4] for calculating the activation energy of the process of removal of adsorption water, which amounted to 28 kJ/mole, and the energy of removal of chemically bound water from kaolinite, which was 89 kJ/mole. Berlin clay belongs to the medium-plastic category. The pycnometric density of the clay in the natural state is 2.53 g/cm<sup>3</sup>. The clay is moderately sinterable at a moderate temperature.

In order to determine the heating behavior of Vishnevogorskoe and Chupinskoe pegmatites, these materials were preliminarily crushed (no residue on screen

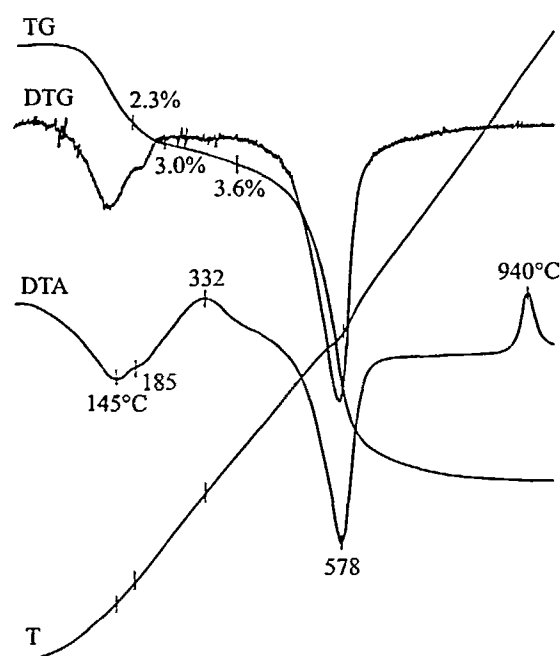


Fig. 1. Thermogram of a sample of Berlin clay.

<sup>1</sup> Ural State Engineering University, Ekaterinburg, Russia;  
Ekaterinburg Ceramic Plant, Ekaterinburg, Russia;  
Institute of High-Temperature Electrochemistry of the Ural Branch of the  
Russian Academy of Sciences, Ekaterinburg, Russia.

TABLE 1

Material	Mass fraction, %							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	loss after calcination
Berlin clay	49.50	31.70	3.90	0.92	0.75	0.78	0.20	11.80
Chupinskoe pegmatite	70.80	17.40	0.18	0.62	0.30	6.70	3.30	0.34
Vishnevogorskoe pegmatite	64.00	20.30	0.26	0.83	0.58	5.80	7.10	0.78

TABLE 2

Composition, %	Mixture	Mass fraction, %*							
		SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	loss after calcination
50% Berlin clay, 50% Chupinskoe pegmatite	M-1	60.15	24.55	2.04	0.77	0.52	3.74	1.75	6.07
		64.03	26.13	2.17	0.82	0.55	3.98	1.86	—
30% Berlin clay, 70% Chupinskoe pegmatite	M-2	64.41	21.69	1.29	0.71	0.43	4.92	2.37	3.77
		66.93	22.54	1.34	0.74	0.44	5.11	2.46	—
50% Berlin clay, 50% Vishnevogorskoe pegmatite	M-3	56.75	26.00	2.08	0.87	0.66	3.29	3.65	6.29
		60.56	27.74	2.22	0.93	0.70	3.51	3.89	—
40% Berlin clay, 60% Vishnevogorskoe pegmatite	M-4	58.20	24.86	1.72	0.90	0.65	3.80	4.34	5.19
		61.38	26.22	1.81	0.95	0.68	4.00	4.66	—

\* The numerators present the chemical composition of the mixture in the natural state, the denominators give the data recalculated for calcined substance.

TABLE 3

Mixture	SiO <sub>2</sub> : Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O + Na <sub>2</sub> O
M-1	2.45	5.84
M-2	2.97	7.57
M-3	2.18	7.40
M-4	2.34	8.66

No. 006). The obtained powders were used for fabricating disc specimens 10 mm in diameter and 7 mm high. The specimens were fired in a furnace with silicon carbide heaters in the temperature range of 1050–1300°C. At 1200°C, the edge of the specimens fabricated from Vishnevogorskoe pegmatite melted; in specimens of Chupinskoe pegmatite, the same occurred at 1300°C. Melting was observed for all specimens and was more considerable in specimens from the Vishnevogorskoe pegmatite.

The blend and chemical compositions of the tested mixtures are presented in Table 2, the ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> and the total amount of alkaline oxides are presented in Table 3.

The data in Table 3 show that the mixtures based on Berlin clay and Chupinskoe pegmatite possess a lower content of alkaline oxides (5.84–7.57%) and a higher ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> (2.45–2.97) than the mixtures based on Berlin clay and Vishnevogorskoe pegmatite (7.40–8.66 and

2.18–2.34, respectively). This gave us grounds for assuming that mixtures with Chupinskoe pegmatite would be less deformable in firing and sinter at a higher temperature than mixtures with Vishnevogorskoe pegmatite.

The technology for fabricating the specimens was as follows. The initial raw components were batched, subjected to wet milling for 6 h to a residue of at most 2% on screen No. 006. The prepared slip was dehydrated, the resulting mixture dried to a moisture content of 6%, then milled and screened through screen No. 05 until the residue disappeared. The obtained powder was shaped into disc specimens 36 mm in diameter and 10 mm high under a pressure of 25 MPa. The specimens were dried under laboratory conditions and fired in a furnace with silicon carbide heaters at 900–1250°C with an interval of 50°C.

The degree of sintering of the studied specimens is presented in Fig. 2 and Table 4.

The most intense sintering was observed in the temperature range of 1000–1150°C. The mixtures with Vishnevogorskoe pegmatite (M-3 and M-4) sintered fully at 1200°C, whereas the mixtures with Chupinskoe pegmatite sintered fully at 1250°C. Specimens with Vishnevogorskoe pegmatite (composition M-4) fired at 1250°C bear traces of burning (bulging, presence of closed porosity). Specimens of mixture M-1 (50% Berlin clay + 50% Chupinskoe pegmatite) fired at 1250°C had the best quality.

TABLE 4

Firing temperature, °C	Mixture	Linear shrinkage, %	Water absorption, %	Apparent density, g/cm <sup>3</sup>	Porosity, %		
					open	closed	true
900	M-1	0.68	19.50	1.70	33.30	Not determined	
	M-2	0.39	23.60	1.58	36.85		
	M-3	0.60	19.00	1.69	32.00		
	M-4	0.76	24.20	1.62	39.10		
1000	M-1	1.55	19.90	1.71	34.03	The same	
	M-2	0.60	23.25	1.58	36.75		
	M-3	4.70	17.71	1.76	31.20		
	M-4	2.90	19.40	1.70	33.00		
1100	M-1	8.90	9.05	2.00	18.02	The same	
	M-2	5.52	11.10	1.90	20.94		
	M-3	10.96	4.79	2.11	10.14		
	M-4	12.20	5.21	2.13	11.08		
1150	M-1	10.54	6.67	2.11	13.95	The same	
	M-2	13.30	1.87	2.27	4.24		
	M-3	12.20	0.85	2.41	2.06		
	M-4	13.90	1.55	2.27	3.53		
1200	M-1	13.62	3.85	2.26	8.72	1.08	9.80
	M-2	14.00	0.64	2.31	1.48	6.72	8.20
	M-3	11.52	0	2.41	0	3.60	3.60
	M-4	15.30	0	2.32	0	9.60	9.60
1250	M-1	14.50	0	2.39	0	2.40	2.40
	M-2	12.43	0	2.25	0	7.60	7.60
	M-3	9.46	0	2.32	0	6.90	6.90
	M-4	1.01	0	1.75	0	29.00	29.00

TABLE 5

Phase	Mass fraction, %, in the composition			
	M-1	M-2	M-3	M-4
Mullite	22.82	14.52	19.64	14.49
Glass phase	62.95	78.51	79.90	85.11
Free SiO <sub>2</sub>	13.80	6.53	—	—

TABLE 6

Temperature range, °C	TCLE, 10 <sup>-6</sup> °C <sup>-1</sup> , of specimens of			
	M-1	M-2	M-3	M-4
20 – 100	4.05	4.70	3.65	3.80
20 – 200	4.90	5.45	4.25	4.90
20 – 300	5.40	5.85	4.90	5.15
20 – 400	5.50	6.30	5.35	5.45
20 – 500	6.35	6.85	5.65	5.60
20 – 600	6.95	7.20	5.75	5.85

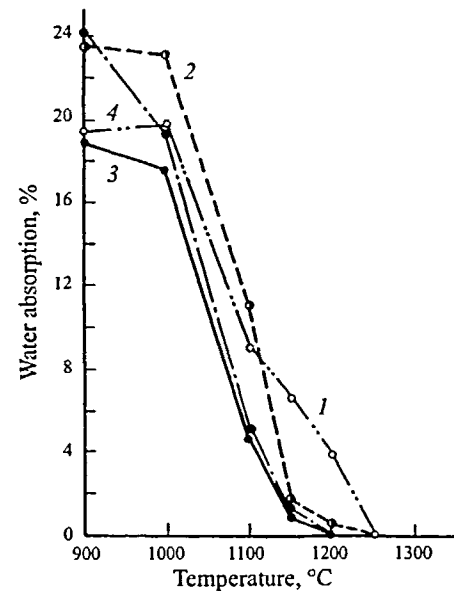


Fig. 2. Dependence of water absorption on the firing temperature of specimens of mixtures M-1 (1), M-2 (2), M-3 (3), and M-4 (4).

The phase composition of the specimens was studied by the x-ray method using a DRON-3 installation equipped with a computer and an US RDS data base. Specimens of mixture M-1 fired at 1250°C and mixture M-3 fired at 1200°C were photographed at angles ranging from 10 to 85°.

Deciphering of the x-ray patterns showed that the predominant crystalline phases in M-1 and M-3 ceramics were mullite  $2\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and low-temperature quartz.

In addition, we calculated the compositions of specimens of mixtures M-1, M-2, M-3, and M-4 fired at 1200°C by the method in [5]. The results are presented in Table 5.

It can be seen that the phase composition of material M-1 is represented by mullite, free  $\text{SiO}_2$  and a glass phase; the phase composition of material M-3 (calculated) is represented by mullite and a glass phase. As a result of x-ray phase analysis of mixture M-3 we established the presence of free  $\text{SiO}_2$  as well. The difference in the data obtained is explainable by the fact that the method in [5] envisages prolonged firing of ceramic materials (stronger dissolution of  $\text{SiO}_2$  in the feldspar melt). In the case of the rapid firing regimes used in our work, the degree of dissolution of  $\text{SiO}_2$  in the feldspar melt was much less, and therefore the x-ray phase analysis of mixture M-3 showed the presence of free  $\text{SiO}_2$ .

We also conducted dilatometric measurements using a DKV-4 vertical differential quartz dilatometer. The tested specimens were rods  $10 \times 10 \times 70$  mm in size fabricated by semidry molding under a pressure of 25 MPa and fired at 1250°C (compositions M-1 and M-2) and 1200°C (compositions M-3 and M-4). The temperature coefficients of linear expansion of the specimens are presented in Table 6.

The value of the TCLE of a ceramic material depends on its phase composition. The data in Table 6 show that specimens of M-1 and M-2 have a higher TCLE. The content of free  $\text{SiO}_2$  in them is higher than in specimens of M-3 and M-4.

In order to study the microstructure the specimens were polished. The microstructure was studied using a vertical metallographic MIM-7 microscope in a reflected light with magnification of  $\times 170$ . We tested specimens of mixtures M-1 and M-2 fired at  $1250^\circ\text{C}$  and specimens of M-3 and M-4 fired at  $1200^\circ\text{C}$ . The specimens had a certain closed porosity (see Table 4). The latter was higher in the specimens based on Berlin clay and Vishnevogorskoe pegmatite, i.e., at most 9.6% (composition M-4). The closed pores were distributed uniformly over the whole of the surface of the specimens. The minimum pore size was about  $3\text{ }\mu\text{m}$ , the maximum size was  $15\text{ }\mu\text{m}$ .

Thus, Berlin clay and Chupinskoe and Vishnevogorskoe pegmatites can be used for fabricating fully sintered materi-

als at  $1200^\circ\text{C}$  (Vishnevogorskoe pegmatite) and  $1250^\circ\text{C}$  (Chupinskoe pegmatite).

After firing and polishing, the specimens have an attractive appearance and good technical properties (high abrasion and mechanical strengths). The results of the given work can be used for developing new compositions of mixtures for manufacturing floor tile.

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